

4.0.1.3 Manufacture

The methylamines are made by reacting methanol and ammonia in a continuous-flow system in the presence of a dehydration catalyst, followed by the separation of unreacted raw materials and the mono-, di- and trisubstituted methylamines.

Methanol (1 mole) and ammonia (2 moles) are mixed and pumped through a preheated or heat exchanger (at 200 psi), and heated to 350°C. The vapors then pass to a reaction chamber containing an alumina-gel catalyst, where amination takes place at about 450°C. Space velocity may vary but is usually in the vicinity of 1,000 reciprocal hours. The crude methylamines leaving the reaction chamber contain unreacted methanol and ammonia as well as smaller amounts of by-products (carbon dioxide and formaldehyde).

The reaction mixture passes through a cooler and thence to a rectifying column, operated under reaction pressure (200 psi), in which ammonia is removed as overhead for reuse. An ammonia-free amine mixture leaves the bottom of the column. This mixture contains all three methylamines in proportions depending on the reaction conditions chosen. Under the conditions stated, the mixture will be essentially as follows: monomethylamine, 50 mole per cent; dimethylamine, 20 mole percent; trimethylamine, 30 mole percent. The boiling points of the three amines are quite close, and hence the amines are difficult to separate by fractionation.

Bottoms from the ammonia column are fed to a second or trimethylamine column where by extractive distillation with water, pure trimethylamine is removed overhead, and in a fourth dimethylamine is separated from water and high boiling impurities.

If larger proportions of dimethylamine or trimethylamine are desired, the ratio of these products to monomethylamine may be increased by recycling the lower amine and by reducing the ammonia-methanol ratio. When monomethylamine is the desired product, either water or trimethylamine is added to the feed to reduce formation of di- and trimethylamines.

A similar process is operated at 90 psi and 700°F. Water is first removed from the condensed crude product in a low-pressure stripper (75 psi). The overhead is compressed to 250 psi, and the products separated as previously described.

Higher amines

The higher amines, ethyl- through amyl-, may also be made by processes similar to that described for the methylamines. Either dehydration catalysts (such as alumina) or hydrogenation catalysts may be used, the latter in conjunction with hydrogen. When hydrogenation catalysts such as nickel are used, which are susceptible to high temperatures, the reaction is run at higher pressures in the liquid phase.

An example of conditions used in the butylamine process by passing butanol, ammonia, and hydrogen over a hydrogenation catalyst is as follows: catalyst-pelleted nickel, temperature - 190°C; space velocity-2,250 reciprocally hours; molar percentage in feed-7.5 percent butanol, 45 per cent ammonia, 43 per cent hydrogen; overall conversion-86.3 percent (24.4 percent mono-, 46.7 percent di-, and 15.2 conversion to tributylamine is 2.4 percent. Overall yield to amines after butanol recovery is 91.6 per cent. When hydrogen is not used in the manufacture of higher amines, a large part of the alcohol is converted to the nitrile.

4.0.2 From alkyl chloride and ammonia

[Example: Amylamine]

4.0.2.1 Raw materials

Basis- 1 ton amylamines (mixed)	
Mixed amyl chlorides	2500 lb
Caustic soda (solid)	975 lb
Ammonia	360 lb
Ethyl alcohol (loss)	Small

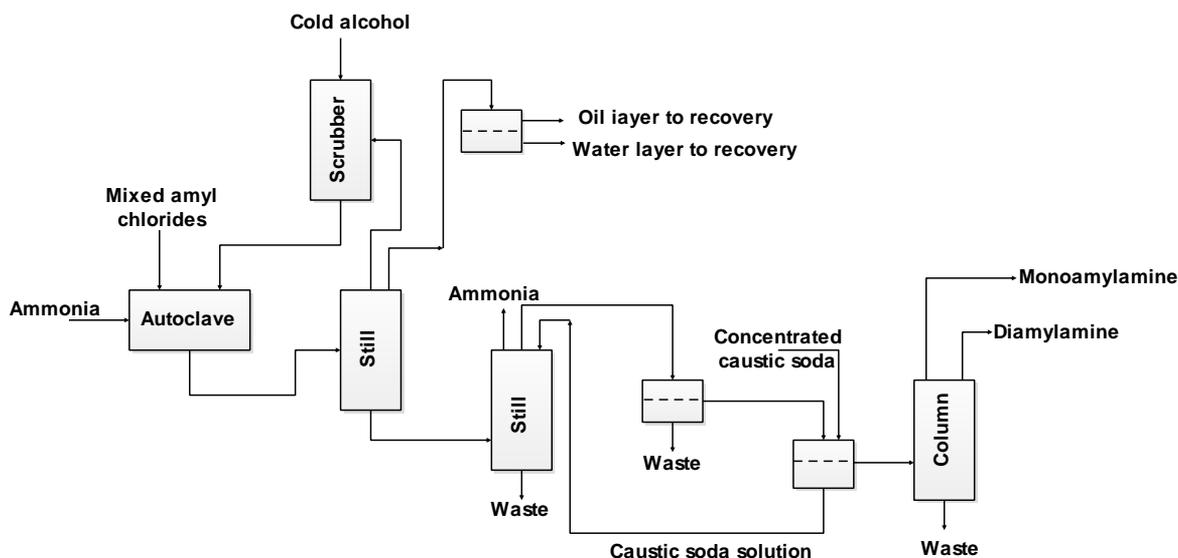
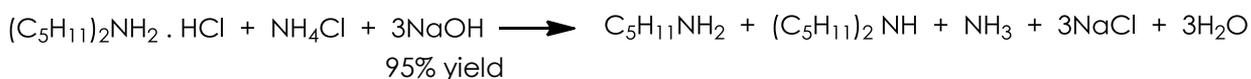


Figure: Production of Amylamine from alkyl chloride and ammonia

4.0.2.2 Reaction



4.0.2.3 Manufacture

A mixture of alcoholic ammonia and mixed amyl chlorides (distillation 95 per cent between 85 and 109°C) is pumped to an autoclave, where it is further mixed with anhydrous ammonia. Temperature of the reacting mixture is maintained at 160 to 165°C for 2hr, after which the temperature is raised until the autoclave pressures reaches 400 psi, under which conditions the contents of the reactor are held for an additional 2 hr. The pressure is released, and the autoclave contents are discharged to a still operating at pressure below 7 psi. Here ammonia is recovered through a reflux system attached to a series of scrubbers in which ammonia is retained in cold alcohol and used for the next batch of amine.

When the ammonia present in the contents of the still has dropped to less than 1 per cent, by-product amylene and amyl alcohols, unreacted amyl chloride and ethyl alcohol, and traces of mines are distilled over head until the distillate consists only of water. The condensed distillate is mixed with more water thus forming two liquid layers, the aqueous and oil layers are separated and sent to separate fractionation and recovery systems.

The residue remaining in the still, consisting essentially of amine hydrochlorides, is sent to a second still, where a caustic-soda solution is added to liberate the amines from their salts. Some liberated ammonia is then distilled overhead, followed by wet amylamines. On condensation of the amine vapors, most of the accompanying water separates. The oil layer (wet amylamines) is separated in a decanter and pumped to an agitated vessel for dehydration with concentrate caustic soda. The caustic layer is returned to the still for amine liberation, and the dry amylamines go to a rectifying column for fractionation.

The product consists of 3 parts monoamylamines and 2 parts of disamylamines. Very little of trimethylamines found. 2-ylamines may be made by reacting diamylamines with mixed amyl chlorides and caustic soda in the autoclave mentioned previously for 4 hr at 205 to 210°C. The separation equipment used for mono-and diamylamines may be used to recover triamylamines by steam distillation followed by vacuum fractionation.

4.0.3 From aldehyde and ammonia

The patent literature indicates that alkylamines can be produced by passing aldehydes, ammonia, and en over a hydrogenation catalyst. In one example, a

butyraldehyde-butyrilimine mixture (made by reacting butyraldehyde and ammonia) is mixed with fifteen times its weight of ammonia and reacted with hydrogen at 500 psi and 150°C. The catalyst is then removed, the excess ammonia distilled, and pure butylamine recovered in a 90 per cent yield based on the original butyraldehyde.

Uses

	Per cent
➤ Monomethylamine	
Herbicides and fungicides	60
Surface-active agents	15
Miscellaneous	<u>25</u>
	100
➤ Dimethylamine	
Solvents for textile spinning	31
Unsym. dimethyl hydrazine	22
Surface-active agents	16
Herbicides and fungicides	13
Rubber accelerators	13
Miscellaneous	<u>05</u>
	100
➤ Trimethylamine	
Chlorine salts	85
Miscellaneous	<u>15</u>
	100
➤ Ethylamines	
Rubber chemicals	48
Agricultural chemicals	24
Miscellaneous	<u>28</u>
	100
➤ Isopropylamines	
Agricultural chemicals	54
Surface-active agents	20
Rubber chemicals	14
Miscellaneous	<u>12</u>
	100
➤ Butyl amines	
Rubber chemicals	76
Miscellaneous	<u>24</u>
	100

4.1 DIMETHYLFORMAMIDE

4.1.1 Introduction

Formamides are derivatives of the smallest of the aliphatic carboxylic acids, formic acid, and are thus structurally and chemically rather straight forward substances. Two of the simplest members of the family—formamide itself HCONH_2 , and N, N-dimethylformamide $[\text{HCON}(\text{CH}_3)_2]$ have considerable industrial importance because of their chemical bifunctionality and high polarity. Formamide is especially valued for its chemical reactivity; N, N-dimethylformamide is used widely for its solvent properties.

4.1.2 Physical properties

Dimethylformamide is the organic compound with the formula $[(\text{CH}_3)_2\text{NC}(\text{O})\text{H}]$. Commonly abbreviated DMF, this colourless liquid is miscible with water and the majority of organic liquids. DMF is a common solvent for chemical reactions. Pure dimethylformamide is odorless whereas technical grade or degraded dimethylformamide often has a fishy smell due to impurity of dimethylamine. Its name is derived from the fact that it is a derivative of formamide, the amide of formic acid.

Dimethylformamide is miscible in all proportions with water, alcohols, ethers, ketones, esters, and carbon disulfide, as well as with chlorinated and aromatic hydrocarbons. By

contrast, it has only limited solubility or complete insolubility in aliphatic hydrocarbons. Many high molecular mass natural products and synthetics are quite soluble in DMF. Examples include poly(vinyl alcohol), poly(vinyl chloride), poly(vinylidene chloride), poly(vinyl acetate), poly(vinyl ether), polyacrylate, polyacrylonitrile, polystyrene, polyester resins, alkyd resins, urea-formaldehyde resins, melamine-formaldehyde resins, phenol-formaldehyde resins, epoxy resins, and natural resins. It is also a good solvent for a number of drying oils, plasticizers, and cellulose derivatives, as well as for both natural and chlorinated rubber. Most halogenated hydrocarbons are also soluble in DMF. Various inorganic salts are highly soluble in DMF.

4.1.3 Chemical properties

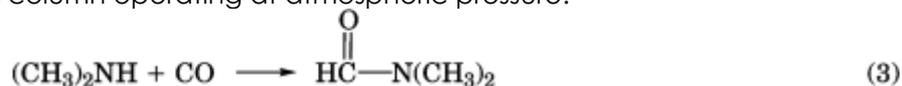
N, N-Dimethylformamide is stable to air and light and, unlike its parent compound formamide, can be distilled without decomposition at atmospheric pressure. Nevertheless, decomposition is observed at temperatures above the boiling point, the products being carbon monoxide and N, N-dimethylamine. The compound also shows fewer tendencies than formamide to hydrolyze. It is hygroscopic, however, and water absorbed from the air will produce traces of hydrolysis products; these produce the faint amine odor that frequently accompanies commercially DMF.

4.1.4 Manufacture

There are two processes used commercially for DMF manufacture. A two-step process involves carbonylation of methanol to methyl formate, and reaction of the formate with dimethylamine.



The methanol carbonylation is performed in the presence of a basic catalyst such as sodium methoxide and the product isolated by distillation. In one continuous commercial process the methyl formate and dimethylamine react at 350 kPa (3.46 atm) and from 110 to 120°C to effect a conversion of about 90%. The reaction mixture is then fed to a reactor-stripper operating at about 275 kPa (2.7 atm), where the reaction is completed and DMF and methanol are separated from the lighter by-products. The crude material is then purified in a separate distillation column operating at atmospheric pressure.



A second process is the direct carbonylation of dimethylamine in the presence of a basic catalyst or a transition metal. This carbonylation is often run in the presence of methanol in order to help solubilize the catalyst, and presumably proceeds through methyl formate as an intermediate. Again, the basic catalyst is typically sodium methoxide, although other bases such as phenoxides and basic anion-exchange resins have also been used. The reaction using sodium methoxide is performed at 4.9 MPa (48 atm) and 120°C.

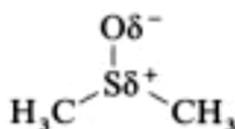
4.1.5 Storage and handling

Pure DMF is essentially non-corrosive to metals; however, copper, tin, and their alloys should be avoided. Ideal materials for its handling and storage are non-alloy (carbon) steels, stainless steels, and aluminum. Seals and other soft materials should be made of polytetrafluoroethylene, polyethylene, or high molecular weight polypropylene. Oils and grease are not suitable as lubricants; however, graphite can be used to lubricate moving parts in contact with DMF. Since DMF is hygroscopic, it should be kept under a blanket of dry nitrogen. High purity DMF required for acrylic fiber production is best stored in aluminum tanks.

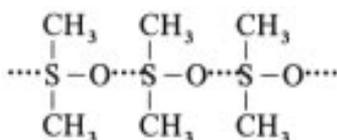
4.1.6 Uses

- The two largest uses for DMF in the United States had been in pharmaceutical processing and acrylic fiber production.
- The combined pharmaceutical applications account for an estimated 25% of DMF consumption. In the pharmaceutical industry, DMF is used in many processes as a reaction and crystallizing solvent because of its remarkable solvent properties.
- Another significant application for DMF is as a solvent for depositing polyurethane coatings on leather and artificial leather fabrics.
- Another use is in various extraction and absorption processes for the purification of acetylene or butadiene and for separation of aliphatic hydrocarbons, which have limited solubility in DMF, from aromatic hydrocarbons.
- DMF has also been used to recover CO₂ from flue gases. Because of the high solubility of SO₂ in DMF, this method can even be used for exhaust streams from processes using high sulfur fuels.
- DMF is used extensively as a solvent, reagent, and catalyst in synthetic organic chemistry.

4.2 DIMETHYL SULFOXIDE

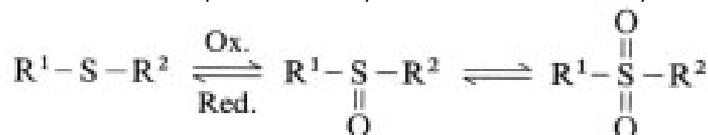


Dimethyl sulfoxide (DMSO) is a colorless, odorless, strongly hygroscopic liquid. It is readily miscible with water and other protic solvents such as alcohols. This property can be attributed to the formation of strong hydrogen bonds between the polarized S–O bond and water molecules. The strong polarity of the S–O bond, with a partial negative charge on oxygen is shown by the high dipole moment and basicity of dimethyl sulfoxide. Pure DMSO forms chain like polymeric association complexes at room temperature. This gives rise to considerably higher melting (18.5°C) and boiling points (189°C) compared to dimethyl sulfide.



4.2.1 Manufacture

In principle, DMSO can be produced by oxidation of dimethyl sulfide.



These methods are, however, often suitable only for small quantities. In industry, DMSO is produced by catalytic oxidation of dimethyl sulfide with oxygen or by oxidation with nitrogen dioxide. The oxidation of dimethyl sulfide with oxygen at 7.2MPa and 105 °C gives good yields of DMSO.

The oldest and most frequently used method for the production of sulfoxides is by oxidation of sulfides. Since further oxidation to the corresponding sulfones can occur, a range of selective reagents and methods has been developed. Oxidation with hydrogen peroxide, which has long been known, can be carried out in the presence of various catalysts. Acids, such as acetic, perchloric, and sulfuric acids, are suitable. A more recent industrial process uses 50% sulfuric acid and an organic acid, such as formic or acetic acid, in a 1:1 ratio as the catalyst.

4.2.2 Uses

Dimethyl sulfoxide is an excellent solvent that is widely used for reactions in modern chemistry. Because of its high polarity and good solvation of cations, DMSO dissolves not

only a large number of organic compounds, but also many metal salts, particularly those of alkali and alkaline-earth metals. DMSO is also a good solvent for many polymers.

4.3 TETRAHYDRO FURAN (THF)

4.3.1 Introduction



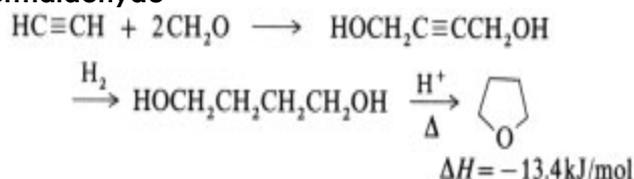
Tetrahydrofuran (THF) tetramethylene oxide, oxolane, is five-membered cyclic ether with wide application in the chemical industry.

4.3.2 Physical properties

Tetrahydrofuran (THF) is a colorless, water-miscible organic liquid with low viscosity at standard temperature and pressure. This heterocyclic compound has the chemical formula $(\text{CH}_2)_4\text{O}$ having melting point (-108.5°C) and boiling point (66°C) . As one of the most polar ethers with a wide liquid range, it is a useful solvent. Its main use, however, is as a precursor to polymers. THF has an odor similar to its chemical cousin, diethyl ether, but is a much less potent anesthetic than diethyl ether.

4.3.3 Manufacture

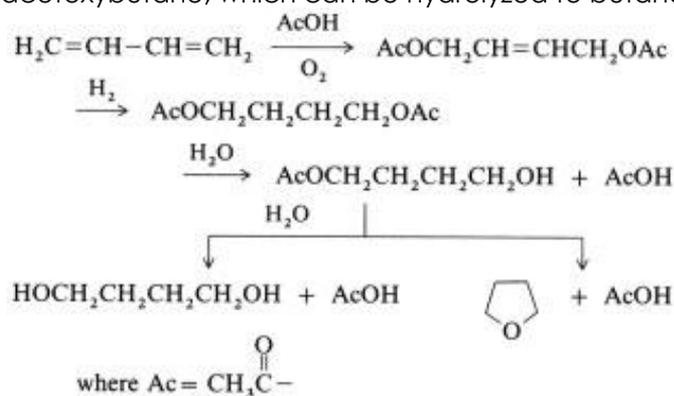
4.3.3.1 Acetylene/Formaldehyde



The process involves a reaction between acetylene and formaldehyde to give 2-butyne-1, 4-diol, with subsequent hydrogenation to 1,4-butanediol. The saturated diol is very readily cyclized to THF with elimination of water by acid catalysis above 100°C . Suitable catalysts include inorganic acids, acidic aluminum silicates, and earth or rare-earth oxides

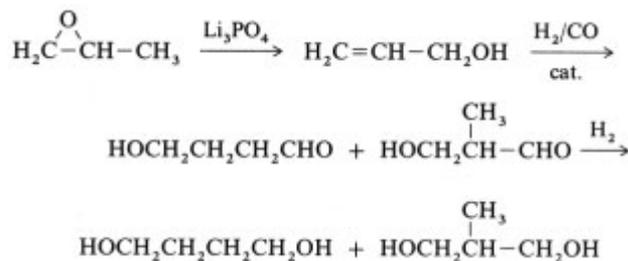
4.3.3.2 Butadiene acetoxylation

Butadiene is oxidized at $3 \text{ MPa}/80^\circ\text{C}$ over a palladium – tellurium catalyst with acetic acid and a nitrogen – oxygen mixture to give 1,4- diacetoxy-2-butene. The olefin is hydrogenated to 1, 4-diacetoxybutane, which can be hydrolyzed to butanediol or THF.



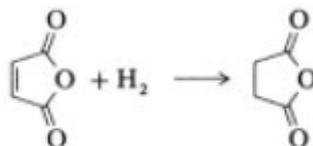
4.3.3.3 Propylene oxide process

Propylene oxide is isomerized to allyl alcohol by conventional means at $250 - 300^\circ\text{C}/1 \text{ MPa}$ over a trilithium orthophosphate (Li_3PO_4) catalyst. The allyl alcohol is then hydroformylated to 4-hydroxybutyraldehyde and the byproduct 3-hydroxy-2-methylpropionaldehyde. Subsequent hydrogenation of the aldehydes gives 1, 4-butanediol as the main product together with 2-methyl-1, 3-propanediol.



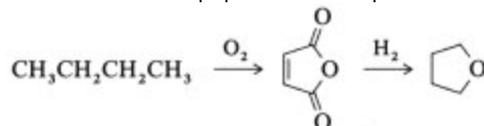
4.3.3.4 Maleic anhydride hydrogenation

Because of its structure, maleic anhydride is an attractive precursor for the preparation of THF.



4.3.3.5 n-Butane – Maleic Anhydride Process

Du Pont has developed a new two-step process for producing THF from n-butane.



The process involves oxidation of n-Butane to maleic anhydride with subsequent hydrogenation of aqueous maleic acid solution over a special palladium catalyst.

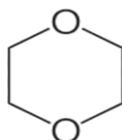
4.3.3.6 Pentosan/Furfural Processes

Because it takes advantage of a renewable raw material, THF production from furfural has attracted interest. Because of their widespread distribution in agricultural waste products, pentosans are especially promising as starting materials. The production of THF from furfural involves catalytic decarbonylation to furan and hydrogenation of the latter to THF.

4.3.4 Uses

- The most important area of application for THF from the standpoint of quantity and turnover is polymerization with simultaneous ring opening to give poly (tetramethylene oxide).
- Available in various molecular masses, this is a key component in the production of important elastic construction materials, thermoplastics and molded elastomers based on polyurethanes, polyesters and polyamides, elastic Spandex fibers, and polyurethane coatings.
- THF is also a versatile solvent for natural and synthetic resins as well as PVC.
- It is used extensively in the varnish and film industries and as a co-solvent for printing inks and adhesives.

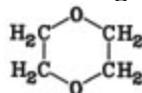
4.4 DIOXANE



1, 4-Dioxane, often called dioxane because the other isomers of dioxane are rare, is a heterocyclic organic compound. It is a colorless liquid with a faint sweet odor similar to that of diethyl ether. It is classified as an ether. This colorless liquid is mainly used as a stabilizer for the solvent trichloroethane. It is an occasionally used solvent for a variety of practical applications as well as in the laboratory.

4.4.1 Physical properties

1, 4-Dioxane, $C_4H_8O_2$, is an extraordinary solvent, capable of solubilizing most organic compounds, water in all proportions, and many inorganic compounds. Dioxane is a cyclic diether forming a six membered ring with the following structure:



Synonyms for dioxane are p-dioxane, diethylene oxide, diethylene dioxide, diethylene ether, 1,4-dioxacyclohexane, dioxyethylene ether, and dioxan. At ambient temperature, dioxane is a clear liquid with an ether-like odor. Its relative stability is similar to other aliphatic ethers, and it forms peroxides on exposure to air as they do. In spite of its exceptional solvent properties, its largest use is in stabilizing 1, 1, 1-trichloroethane and keep it from reacting with aluminum.

Infinite solubility in dioxane can be expected from lower molecular mass aliphatic and aromatic liquid hydrocarbons, ethers, alcohols, ketones, and chlorinated hydrocarbons. Dioxane has solubility for animal and vegetable oils, paraffin oils, synthetic and natural resins, and some inorganic compounds and elements, such as iron chlorides, mercuric chloride, hydrochloric, sulfuric, and phosphoric acids, bromine, chlorine, and iodine.

4.4.2 Manufacture

1, 4-Dioxane is manufactured commercially by dehydration and ring closure of diethylene glycol. Concentrated sulfuric acid (5%) is used as a catalyst, although phosphoric acid, p-toluenesulfonic acid, and strongly acidic ion-exchange resins are recognized alternatives. Operating conditions vary; temperatures range from 130 to 200°C and pressures range from a slight pressure to a partial vacuum (25 – 110 kPa). A favorable temperature is reported to be 160°C. The process is continuous, with dioxane vaporized from the reaction vessel. The vapors are passed through an acid trap and two distillation columns to remove water and to purify the product. Yields of 90% are possible.

4.4.3 Uses

- The largest single use of 1,4-dioxane is the stabilization of 1,1,1-trichloroethane against chemical attack by aluminum. The aluminum oxide film prevents the metal from reacting with 1,1,1-trichloroethane until the film is disturbed. When the bare metal contacts 1,1,1-trichloroethane, chlorine is extracted from the solvent to form $AlCl_3$, which causes dehydrohalogenation of 1,1,1-trichloroethane to produce HCl and vinylidene chloride ($CH_2 = CCl_2$). Dioxane is the foremost inhibitor of these reactions. An insoluble dioxane–aluminum chloride complex is formed, which deactivates the catalyst and seals any openings in the Al_2O_3 film.
- Dioxane is used as a solvent in the formulation of inks, coatings, and adhesives, and as solvent for extracting animal and vegetable oils.
- As a chemical intermediate, dioxane reaction products are useful as insecticides, herbicides, plasticizers, and monomers.
- The oxonium complexes of dioxane with salts, mineral acids, halogens, and sulfur trioxide are used as catalysts and as reagents for anhydrous acid reactions, brominations, and sulfonations.
- In the laboratory, dioxane is useful as a cryoscopic solvent for molecular mass determinations and as a stable reaction medium for diverse reactions.
- Historically, dioxane is reported to be valuable in polymer manufacture and as a solvent for natural and synthetic resins, including cellulose derivatives, polyvinyl acetal resins, acrylonitrile – methyl vinyl pyridine copolymers, and others.

4.5 DIETHYL ETHER

Diethyl ether, also known as ethoxyethane or simply ether, $CH_3CH_2-O-CH_2CH_3$, is one of the most important ethers.

4.5.1 Physical Properties

It is a clear, mobile liquid with a sweetish, slightly pungent, characteristic odor. Diethyl ether is completely miscible with common organic solvents, but only partially miscible with water.

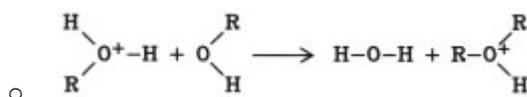
4.5.2 Chemical Properties

- Unsubstituted ethers are chemically very stable. At room temperature, they are neither attacked by alkali metals nor undergo base hydrolysis. They are also resistant to acids, with the exception of hydroiodic acid which cleaves ethers with formation of alkyl iodide; this reaction is the basis of the Zeisel method for the determination of alkoxy groups.
- At higher temperature, ethers are also hydrolyzed by other acids, especially nitric and hydrobromic acids, acyl halides, and phosphorus pentachloride [10]. The rate of hydrolysis increases rapidly with the degree of branching of the alkyl group. Therefore, breakdown or removal of nonvolatile methoxy compounds or methyl-protecting groups by boiling with hydrobromic acid is advantageous.
- At higher temperature, ethers can be cleaved to produce olefins, water, and alcohol, especially in the presence of catalysts such as aluminum oxide.
- Ethers react more quickly with chlorine or bromine than do the corresponding alkanes, substitution taking place mainly in the α -position. Mono- as well as bis (1-haloalkyl) ethers can be obtained by appropriate control of the reaction.
- Ethers form peroxides in the presence of atmospheric oxygen, especially when exposed to light. This has long been known because violent explosions can occur toward the end of ether distillations due to the peroxides present in the distillation residue.

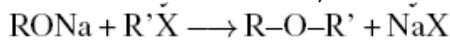
4.5.3 Manufacture

Ethers are generally prepared by catalytic dehydration of alcohols or by reaction of alkyl halides with alkoxides

- Catalytic dehydration of alcohols in the liquid phase. Acids (particularly sulfuric acid) and electrophilic metal and nonmetal halides are effective catalysts for dehydrating alcohols in the liquid phase to produce ethers. Moderately strong acids and salts of weak bases and strong acids are most effective but favorable results are obtained only for the lower alcohols (1 – 3 carbon atoms). The reaction proceeds via intermediate formation of an oxonium compound:



- Catalytic dehydration of alcohols in the gas phase over, e.g., aluminum oxide, anhydrous alumina, or bauxite at a temperature of 180 – 250 °C gives ether yields of up to 75 %.
- Reaction of alkyl halides with alkali-metal alkoxides by the Williamson synthesis:

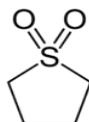


- Introduction of dimethyl sulfoxide as a solvent considerably improved yields in the Williamson ether synthesis [20]. A mixture of sodium hydroxide and alcohol can be used in place of the alkoxide.

4.5.4 Uses

- Diethyl ether is a good solvent for many oils, fats, resins, alkaloids, odorants, and dyes and, therefore, is widely used as a solvent and as an extractant.
- When mixed with ethanol, diethyl ether is used to gel nitrocellulose and to dissolve collodion wool.
- Ether is used as a reaction medium in the laboratory and in industry due to its chemical stability, low boiling point, and solvent properties for organometallic compounds (Grignard reagents).
- It is also employed as an anesthetic in medicine.

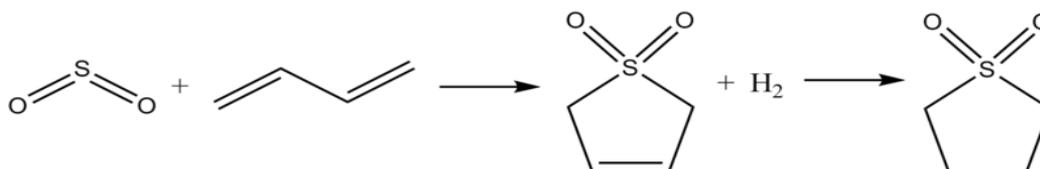
4.6 SULFOLANE



Sulfolane (also tetramethylene sulfone, systematic name: 2,3,4,5-tetrahydrothiophene-1,1-dioxide) is a clear, colorless liquid commonly used in the chemical industry as an extractive distillation solvent or reaction solvent. Sulfolane was originally developed by the Shell Oil Company in the 1960s as a solvent to purify butadiene. Sulfolane is an aprotic organosulfur compound, and it is readily soluble in water.

4.6.1 Manufacture

The original method developed by the Shell Oil Company was to first allow butadiene to react with sulfur dioxide. This yields sulfolene, which was then hydrogenated using Raney nickel as a catalyst to give sulfolane.



Shortly thereafter, it was discovered that both the product yield and the lifetime of the catalyst could be improved by adding hydrogen peroxide and then neutralizing to a pH of roughly 5-8 before hydrogenation. Recently, it was found that Ni-B/MgO showed superior catalytic activity to that of Raney nickel and other common catalysts that have been used in the hydrogenation of sulfolene.

Other syntheses have also been developed, such as oxidizing tetrahydrothiophene with hydrogen peroxide. This first produces tetramethylene sulfoxide, which can then be further oxidized to tetramethylene sulfone. Because the first oxidation takes place at low temperature and the second at higher temperature, the reaction can be controlled at each stage. This gives greater freedom for the manipulation of the reaction, which can potentially lead to higher yields and purity.

4.6.2 Uses

Sulfolane is widely used as an industrial solvent, especially in the extraction of aromatic hydrocarbons from hydrocarbon mixtures and to purify natural gas. Pyrrolidones became available industrially through the fundamental work of W. REPPE on acety chemistry. He synthesised butynediol and from it *v*-butyrolactone, the starting material for the commercial production of pyrrolidones.

4.7 ALKYL PYRROLIDONE

4.7.1 2-pyrrolidone

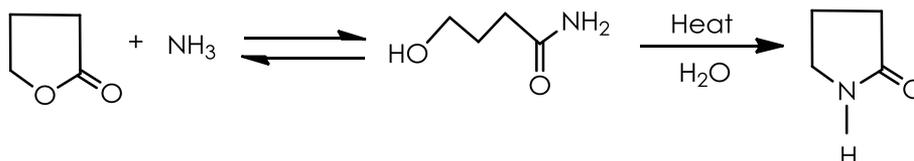
2-Pyrrolidone, pyrrolidone, 2-pyrrolidinone, *v*-butyrolactam, C₄H₇NO, is a colorless, hygroscopic lie above its meeting point. It is miscible with water and common organic solvents, but not with aliphaticcyclicaliphatic hydrocarbons.

4.7.1.1 Manufacture

2-Pyrrolidone can be produced by the following methods:

- Catalytic or electrochemical reduction of succinimide.
- Carbonylation of allylamine
- Hydrogenation of succinic acid dinitrile under hydrolytic conditions
- Reaction of maleic or succinic anhydride in aqueous ammonia with Pd-Ru catalysts.

Industrially, 2-pyrrolidone is almost exclusively produced by reacting aqueous *v*-butyrolactone with ammonia:



Formation of the undesired 4-(N-2-pyrrolidonyl)butyramide can be suppressed if the two stage reaction is carried out in the gas phase on a magnesium silicate catalyst (250-290°C, 0-1.4 MPa)

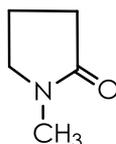
4.7.1.2 Handling, Storage, and Transportation

2-Pyrrolidone is transported in steel drums. Other materials suitable for storage and transportation a aluminum and stainless steel. Moisture must be excluded. 2-Pyrrolidone can be kept for ca. 1 year closed containers. 2-Pyrrolidone is not self-igniting or explosive, but is flammable.

4.7.1.3 Uses

Over 95% of the 2-pyrrolidone produced is processed into N-vinyl-2-pyrrolidone. It is also used in the pharmaceutical industry for the production of pyrrolidone nootropics, especially piracetam. 2-Pyrrolidone is also used as a solvent and reaction medium since it is high boiling, inert, and noncorrosive. It can be used to decolorise kerosene and other hydrocarbons. Aromatic hydrocarbons can be extracted from petroleum with 2-pyrrolidone. In the polish and cleaning materials industry it is added to styrene acrylate copolymer dispersions as a film-forming agent.

4.7.2 N-methyl-2-pyrrolidone



N-Methyl-2-pyrrolidone (NMP) N-methylpyrrolidone, 1 -methyl-2-pyrrolidone, C₅H₉NO, is an important, versatile solvent and reaction medium for the chemical industry because of its favorable properties.

4.7.2.1 Manufacture

Large-scale production of NMP is predominately carried out by reacting γ -butyrolactone with methylamine in a shaft reactor (high-pressure tube with special baffles) at 200-350°C and ca. 10 MPa.

Other processes also analogous to those used for pyrrolidone synthesis can also be used, in particular hydrogenation of N-methylsuccinimide or mixtures of maleic or succinic anhydride and methylamine. NMP can also be produced by hydrogenation of N-hydroxymethyl-2-pyrrolidone or by reaction of acrylonitrile with methylamine in the presence of a peroxide radical initiator.

4.7.2.2 Quality specifications and analysis

Technical-grade NMP has the following specifications (gas chromatography): NMP content, min. 99.5wt%; methylamine, max.0.02 wt%; water, max. 0.1 wt% (Karl Fischer titration); color index, APHA 50 max. For special areas of use (e.g.,electronics) higher purities are supplied with the following specifications: methylamine, max. 0.01 wt%; water, max. 0.05 wt%.

4.7.2.3 Handling, Storage, and Transportation

NMP is transported in tank cars or trailers and in drums. Transport and storage containers are generally made of mild steel. Stainless steel, nickel, and aluminum are also suitable as container and drum materials. Small quantities can be stored in polyethylene, polypropylene, or clear glass bottles. NMP shows unlimited shelf life in tightly closed containers, slight discoloration does not impair its quality. It is flammable.

4.7.2.4 Uses

NMP is an important solvent because of its low volatility, thermal stability, high polarity, and aprotic, noncorrosive properties. Its favorable toxicological and ecological properties account for the fact that NMP is replacing other solvents such as chlorinated

hydrocarbons.

The most important areas of use are

- Petro chemical processing: Acetylene recover)' from cracked gas, extraction of aromatics and butadiene, gas purification (removal of CO₂ and H₂S), lube oil extraction.
- Engineering plastics. Reaction medium for the production of high-temperature polymers such as polyethersulfones, polyamideimides, and polyaramids.
- Coatings: Solvent for acrylic and epoxy resins, polyurethane paints, waterborne paints or finishes, printing inks, synthesis/diluent of wire enamels, coalescing agent.
- Agricultural chemicals: Solvent and /or co-solvent for liquid formulations.
- Electronics: Cleaning agent for silicon wafer, photoresist stripper, auxiliary in printed circuit board technology
- Industrial and domestic cleaning. Component in paint strippers and degreasers e.g., removal of oil, fat, and soot from metal surfaces, carbon deposits and other tarr>' polymeric residues in combustion engines.

4.7.2.5 Environmental aspects

NMP is nontoxic to most aquatic life and shows good biodegradability. The most important data: BOD 1100 mg/g NMP (DIN 38409 part 51), COD 1600 mg/g NMP (DIN 38 409 part 41), TOC (iorganic carbon) 600 mg/g NMP (DIN 38 409 part 3), biodegradability: > 90% DOC (dissolved organic carbon) degradation.

4.7.2.6 Toxicology and occupational Health

N-Methylpyrrolidone is only slightly toxic if ingested or inhaled. LD₅₀ values are 3.5 mL/kg-4.3 g/kg (rat, oral); 7.5 mL/kg (mouse, oral); 3.5 g/kg (rabbit, oral); 2.2 mL/kg (rat, i.v.); 2.4 mL/kg (rat, i.p.); 1.9 mL/kg (mouse, i.p.), >2.5 g/kg (rat, percutaneous); 4-8 g/kg (rabbit, percutaneous). Inhalation (6-8 hrs.) of a highly enriched or saturated atmosphere at 20 or 50°C produced no symptoms in cats, mice, rats, rabbits or guinea pigs. The LC₅₀ value is > 5.1 mg/L (rat, inhalation, aerosol, 4hrs.).

4.8 BUTYL ETHERS

Of the four butyl ethers only the straight-chain isomer is available in commercial quantities.

n-Butyl ether, CH₃(CH₂)O(CH₂)₃CH₃, is a colorless liquid; mp,- 98°C; bp,142°C; d₄²⁰ 0.7481; d₄²⁰ 0.7704; flash point (open-cup), 100°F; viscosity at 15°C, 0.741 cP; surface tension at 15°C, 23.47 dyn/cm;

Temperature, °C	11.3	29.7	66.8	127.7
Vapor pressure, mm Hg	7.5	14.5	57.04	570.5

It is almost insoluble in water (0.03% by wt, at 20°C) but miscible in ethyl alcohol and ether. Like the other ethers, n-butyl ether forms explosive peroxides which should be removed before distillation. Azeotropes of n-butyl ether are given in Table 1.

Typical specifications are as follows: Color (APHA), 15 max; d₂₀²⁰ 0.768-0.771; distillation range, 137-143°C; acidity (as butyric acid), 0.02 wt %, max; water, 0.10 wt %, max; flash point (open-cup), 100°F.

Other component	Bp, °C	Distillate, wt%	
		n-Butyl ether	Other component
Water	94.1	66.6 ^a	33.4
Acetic acid	116.7	19	81.0
Butyl alcohol	117.6	17.5 ^a	82.5
Butyl alcohol	90.6	35.5 ^a	34.6
Water	90.6	35.5 ^a	29.9

Table:1 Azeotropes of n-Butyl Ether

n-Butyl ether is an excellent extracting agent for use with aqueous systems since its solubility in water is less than 1% that of ethyl ether. It is an important solvent for the Grignard and other reactions that require an anhydrous, inert medium. Since it forms many constant-boiling azeotropes, it is useful for purifying other solvents. It is used in the extraction of

hormones and of thioglycolic acid and is an intermediate in "cold" hair-waving formulations.

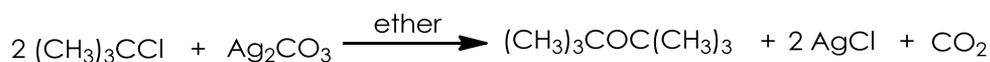
As an ether it undergoes oxidation, cleavage, and nitration. Butyl iodide can be prepared in high yields by heating butyl ether with a mixture of phosphoric acid, phosphorus pentoxide, and potassium iodide; the chloride is obtained in 50% yield by heating with titanium tetrachloride. Dibutyl ether can be aminated in the vapor phase to give 80% amines consisting of mono-, di-, and tributylamines and reacts with ethyl diazoacetate to produce ethyl n-butoxyacetate and butylene. Various simple and mixed chlorobutyl ethers are known. Although butyl ether can be chlorinated, its bis(chloro) ethers are usually made from the chloro alcohol. Thus, bis(4-chlorobutyl) ether is prepared from 4-chlorobutyl alcohol by the sulfuric acid method, or better, by heating furan with phosphorus oxychloride and sulfuric acid.

n-Butyl ether is prepared by dehydration of n-butyl alcohol by sulfuric acid or by catalytic dehydration over ferric chloride, copper sulfate, alum, etc.

sec-Butyl ether is not available commercially but can be prepared by dehydration of sec-butyl alcohol.

Isobutyl ether is not available commercially but has been prepared by dehydration of isobutyl alcohol and by hydrogenation of methallyl ether, $(\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2)_2\text{O}$.

t-Butyl ether, is not a commercial chemical but its synthesis and properties are worth mentioning. The synthesis of di-i-butyl ether was long a vexing problem. Reboul, in 1889, observed that the conventional Williamson technique produced only isobutylene and t-butyl alcohol. Until the early 1940s it was felt that two tertiary butyl groups could not be accommodated by one oxygen atom because of the over crowding of methyl groups. It was finally prepared in 31% yield, by the reaction of i-butyl chloride with silver carbonate in dry ether.



Di-t-butyl ether is a clear, mobile liquid, bp, 108-109°C; n_{D}^{20} 1.3946; d_{20}^{20} 0.7622; heat of combustion at 25°C, 1268.7 kcal/mole; heat of formation at 25°C, 96.2 kcal/mole for the liquid and 87.2 kcal/mole for gas; heat of vaporization, 9.0 kcal/mole.

Unlike the other ethers discussed in this article, i-butyl ether is readily hydrolyzed by dilute acids and gives an immediate Lucas test for i-butyl alcohol, with dilute hydrochloric acid.

t-Butyl ether has an odor reminiscent of camphor. This has been attributed the high steric strain resulting in nearly spherical structure. This strain is approximately 7.6 kcal/mole and is a consequence of the crowding of the opposed meth groups.